A Geochemical Investigation into the Effect of Coal Rank on the Potential Environmental Impacts of CO_2 Sequestration in Deep Coal Beds

Jonathan J. Kolak* and Robert C. Burruss
U.S. Geological Survey, MS 956
12201 Sunrise Valley Drive
Reston, VA, 20192

*corresponding author: jkolak@usgs.gov; 703-648-6750

ABSTRACT

Coal samples of different rank were extracted in the laboratory with supercritical CO_2 to evaluate the potential for mobilizing hydrocarbons during CO_2 sequestration or enhanced coal bed methane recovery from deep coal beds. The concentrations of aliphatic hydrocarbons mobilized from the subbituminous C, high-volatile C bituminous, and anthracite coal samples were 41.2, 43.1, and 3.11 $\mu g\ g^{-1}$ dry coal, respectively. Substantial, but lower, concentrations of polycyclic aromatic hydrocarbons (PAHs) were mobilized from these samples: 2.19, 10.1, and 1.44 $\mu g\ g^{-1}$ dry coal, respectively. The hydrocarbon distributions within the aliphatic and aromatic fractions obtained from each coal sample also varied with coal rank and reflected changes to the coal matrix associated with increasing degree of coalification. Bitumen present within the coal matrix may affect hydrocarbon partitioning between coal and supercritical CO_2. The coal samples continued to yield hydrocarbons during consecutive extractions with supercritical CO_2. The amount of hydrocarbons mobilized declined with each successive extraction, and the relative proportion of higher molecular weight hydrocarbons increased during successive extractions. These results demonstrate that the potential for mobilizing hydrocarbons from coal beds, and the effect of coal rank on this process, are important to consider when evaluating coal beds for CO_2 storage.

INTRODUCTION

There are several potential options available for geologic storage and sequestration of CO_2, including depleted oil and gas reservoirs, coal beds, and formations containing nonpotable, e.g., saline, water. Carbon dioxide storage in depleted oil and gas reservoirs and coal beds is of particular interest because of the potential for concomitant hydrocarbon recovery, e.g., enhanced oil recovery (EOR) and enhanced coal bed methane (ECBM) recovery. Enhanced oil recovery through CO_2 injection is a relatively mature technology that can be economically viable. For example, CO_2-EOR has been practiced at Rangely oil field (Colorado) for roughly 20 years (Klusman, 2003). The use of CO_2 for ECBM recovery is a less mature technology. Field trials have been conducted recently to evaluate the economic viability of this process (Reeves and others, 2002).

The feasibility of CO_2 storage in coal beds as a CO_2 sequestration option is not well defined. Estimates of the ultimate CO_2 storage capacities of deep coal beds have indicated that up to hundreds of gigatons of CO_2 could be stored globally in coal beds (Gentzis, 2000; Herzog, 2001). However, the

ability of coal beds to "permanently" retain injected CO_2 (on the order of hundreds to thousands of years) and the possible geochemical and environmental impacts associated with CO_2 injection are not well known. This dearth of knowledge is due, in part, to an incomplete understanding of the physical and chemical interactions between CO_2 and coal. Several recent studies have targeted these issues through laboratory experiments investigating gas transport and retention within coal samples (Krooss and others, 2002; Karacan, 2003). In addition, a pilot study of CO_2 injection into the San Juan basin (Reeves and others, 2002) has improved our understanding of coal bed reservoir properties. Despite these advances, little is known regarding the fate of CO_2 injected into coal beds or the possible environmental impacts stemming from CO_2 sequestration or ECBM recovery. For example, the pressure-temperature conditions in deep coal beds may render the CO_2 supercritical (Pashin and McIntyre, 2003), and the fate of supercritical CO_2 in this setting is poorly understood. Supercritical CO_2 has physical properties intermediate between those of gaseous CO_2 and liquid CO_2, making it a very effective solvent that is capable of mobilizing (extracting) hydrocarbons from geologic matrices (e.g., Monin and others, 1988). The extent to which hydrocarbons may be mobilized during CO_2-ECBM recovery projects, and the subsequent effect on dissolved hydrocarbon concentrations in produced waters, is unknown.

Coal rank, the collective properties of coal that change during burial and thermal maturation, may exert considerable influence on coal-CO_2 interactions. Recent study has shown that CO_2 storage capacity measured in coal samples varies with coal rank (Gluskoter and others, 2002). Therefore, understanding the effects of coal rank on these interactions may provide essential information for national and global studies of CO_2 storage opportunities in coal-bearing units. To address this matter, we collected ten coal samples, ranging in rank from lignite through anthracite, from several basins in the United States. We report here the findings from three of these samples: a sample of subbituminous C (subC) coal from the Texas Gulf Coast area, a sample of high-volatile C bituminous (hvCb) coal from the Illinois basin (Indiana), and a sample of anthracite (anth) coal from the Appalachian basin (Pennsylvania). These coal samples were extracted with supercritical CO_2, simulating CO_2 storage in deep coal beds. Each coal sample was subjected to multiple extraction events to evaluate the potential for hydrocarbon mobilization during prolonged CO_2 injection in coal beds. The amount and type of hydrocarbons mobilized during simulated CO_2 injections were characterized to evaluate possible environmental impacts of storage of CO_2 in deep coal beds.

METHODS

Sample Collection and Preparation

The Gulf Coast coal sample was subsampled from a core section (Warwick and others, 2000; Warwick and others, 2002). The high-volatile C bituminous and anthracite coal samples were collected as channel samples. All three samples were sent to a commercial lab for grinding, sieving, splitting, and proximate/ultimate analyses (table 1). Petrographic analyses and CO_2 and CH_4 adsorption isotherms were also conducted to characterize each coal sample and determine gas storage capacities (Gluskoter and others, 2002).

Supercritical CO_2 Extraction and Preparative Chromatography

At the U.S. Geological Survey (USGS), additional splits were taken from the coal samples and prepared for extraction with supercritical CO_2 (Kolak and Burruss, 2003). The ground coal samples were dried overnight at 40°C under air in a gravity convection oven to remove moisture. The dried samples were extracted using an ISCO[1] SFX 220 extraction unit coupled to an ISCO 260D syringe pump.

Supercritical fluid extraction-grade CO_2 (no helium headspace) was used in all the experiments. For each experiment, approximately 1.0 g of ground coal sample was weighed into a 10 ml-capacity extraction vessel and spiked with aliphatic and PAH surrogate solutions. The extractions were conducted at 40°C and 100 bar, simulating CO_2 injection in a coal bed located approximately 1 km below the land surface. The extraction program consisted of a 15-minute static (no-flow) step followed by a 60-minute dynamic (flow) step at a flow rate of approximately 1.8 ml CO_2 min^{-1}. The program was designed specifically to produce a solvent:sample ratio (~2.4 moles solvent: 1 g dry coal) comparable to that obtained during a parallel set of extractions using Soxhlet extractors and dichloromethane (Kolak and Burruss, 2003). Hydrocarbons mobilized from the coal sample with supercritical CO_2 were collected in a hexane solvent trap held at 0°C. The samples were subjected to a series of extractions, each successive extraction beginning immediately after completion of the previous one, to evaluate the effects of prolonged CO_2 injection on hydrocarbon mobilization. The hexane solvent trap was changed in between each extraction to monitor changes in the amount and type of hydrocarbons mobilized. The hexane in each trap was subsequently concentrated under a stream of N_2 to a volume of 5 ml.

_____

[1]Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

The extracted hydrocarbons present in the hexane were separated into two compound classes, aliphatics and aromatics, using preparative liquid chromatography. Glass columns (11-mm i.d.) were packed in dichloromethane (DCM) with 1 ml activated copper, 2.5 g neutral alumina (5% water-deactivated), 2.5 g silica 62 (100% activated) and 5.0 g silica 923 (100% activated). The columns were flushed with hexane and then charged with the sample extracts. The aliphatic and aromatic fractions were consecutively eluted from each column using 100% hexane and a 30:70 (v/v) DCM:hexane mixture, respectively. The aliphatic and aromatic fractions were subsequently evaporated under a stream of N_2 to a final volume of 1 ml and 2 ml, respectively. The fractionated extracts were stored in the dark at 4°C until analysis.

Quantitative Analysis of Extracted Hydrocarbons

The fractionated sample extracts were analyzed via gas chromatography-mass spectrometry (GC-MS) using an Agilent 6890 Gas Chromatograph interfaced with an Agilent 5973 Mass Selective Detector. Prior to analyses, perdeuterated *n*-nonadecane was added to the aliphatic fractions as an internal standard to correct for variations in instrument response. Likewise, an internal standard solution containing naphthalene-d$_8$, phenanthrene-d$_{10}$, chrysene-d$_{12}$, and perylene-d$_{12}$ was added to each aromatic sample. For both aliphatic and aromatic fractions, 1 μl of sample extract was injected in the splitless mode and separated on an HP5-MS column (30m x 0.25mm x 0.25μm) using He as a carrier gas (0.9 mL min^{-1}). The following GC oven program was used during the aliphatic hydrocarbon analyses: initial temperature held at 50°C for 1.5 min, followed by a 10°C min^{-1} ramp to 315°C, and held at the final temperature for 15 min. The GC program used for the aromatic hydrocarbon analyses was modified to optimize separation of PAH isomers: the initial oven temperature (50°C) was held for 4.0 min, followed by a 10°C min^{-1} ramp to 150°C, followed by a 6°C min^{-1} ramp to 230°C, followed by a 3°C min^{-1} ramp to 300°C, followed by a 10°C min^{-1} ramp to 310°C, and held at final temperature for 5 min. External standards were run with each batch of samples to generate five-point, concentration-response calibration curves. The response of the m/z 57 ion fragment was used to determine the concentrations of the nC_9-nC_{33} *n*-alkanes, pristane (Pr), and phytane (Ph) in the aliphatic fractions. Concentrations of approximately 30 PAHs, including both parent compounds and alkyl-substituted homologs, were determined using the responses of appropriate target ions (table 2). The members of the naphthalene and phenanthrene homologous series are indicated by the abbreviations NX and PX, respectively, where X = the number of methyl groups (0-4) substituted into the parent compound. The shaded entries (table 2) denote instances

where the total concentration of all isomers associated with a given homolog, e.g., all dimethylnaphthalenes (ΣN2), was determined from the concentration-response curve of a single isomer, e.g., 2,6-dimethylnaphthalene.

RESULTS

Aliphatic Hydrocarbons

The concentrations of target aliphatic compounds, including Pr and Ph, extracted from the coal samples varied with coal rank. The total concentration of aliphatic hydrocarbons (dry coal basis) increased slightly from 41.2 μg g^{-1} in the subbituminous C coal sample to 43.1 μg g^{-1} in the high-volatile C bituminous coal sample. A substantially lower aliphatic hydrocarbon concentration, 3.11 μg g^{-1}, was obtained from the anthracite coal sample. The coal sample extracts also contained branched alkanes, e.g., farnesane, and other alicyclic compounds whose concentrations were not determined in this study. In addition to total aliphatic hydrocarbon concentrations, the distribution of aliphatic hydrocarbons within each sample extract varied considerably with coal rank (fig. 1). For example, the aliphatic hydrocarbons in the subbituminous C extract consisted largely of the higher molecular weight n-alkanes, most notably the nC$_{27}$, nC$_{29}$, and nC$_{31}$ homologs. Conversely, the high-volatile C bituminous coal sample extract contained comparatively lower concentrations of these higher molecular weight n-alkanes, but had greater levels of the lower molecular weight n-alkanes (nC$_{10}$-nC$_{17}$). Pristane is the most abundant aliphatic constituent in this sample extract. The supercritical CO_2 extract from the anthracite sample contained very low concentrations, <0.50 μg g^{-1}, of individual n-alkanes from nC$_9$ though nC$_{20}$. Unlike the other two coal samples, the anthracite sample extract contained no detectable concentrations of higher molecular weight n-alkanes (>nC$_{20}$).

Analyses of hydrocarbon concentrations from consecutive extractions revealed that the high-volatile C bituminous coal sample, in particular, continued to yield appreciable levels of aliphatic hydrocarbons even after several extractions with supercritical CO_2. The hydrocarbon concentrations declined with each successive extraction, however, this decline was relatively more pronounced in the lower molecular weight n-alkanes than in the higher molecular weight n-alkanes (fig. 2). Alkanes >nC$_{24}$ exhibited an even more gradual relative decline in concentration. As a result, there was a gradual shift in the n-alkane distribution between the first and final extractions. For example, the concentration of n-nonane (nC$_9$) in the high-volatile C bituminous coal sample extract decreased from 0.39 μg g^{-1} dry coal (first extraction) to below detectable limits (fourth extraction), whereas n-tetracosane (nC$_{24}$) concentrations in the first and fourth extracts were 1.26 and 0.72 μg g^{-1} dry coal, respectively. Similar behavior was observed during consecutive extractions of the subbituminous C and anthracite coal samples, however, the hydrocarbon levels from these two samples rapidly declined below detection limits in subsequent extracts.

Aromatic Hydrocarbons

Concentrations of PAHs in the coal sample extracts varied with coal rank, increasing from 2.19 μg g^{-1} dry coal in the subbituminous C coal sample extract to 10.1 μg g^{-1} dry coal in the high-volatile C bituminous coal sample extract. The anthracite sample yielded the fewest PAHs: 1.44 μg g^{-1} dry coal. The vast majority of extracted PAHs for all three samples consisted of compounds with four or fewer aromatic rings. Larger PAH compounds, e.g., B[b]f and Icp, were detected in the subbituminous C coal sample extract, but at levels below reporting limits. The extracts from the subbituminous C and anthracite

coal samples have fairly similar PAH distributions, with alkylnaphthalenes and alkylphenanthrenes the dominant species (fig. 3). In both sample extracts, the naphthalene homolog concentration increases with increasing degree of alkyl substitution. The P1 and P3 homologs are the most abundant phenanthrenes in both extracts; the P2 homologs are present at slightly lesser concentrations. The biggest disparity between PAH distributions from these two samples is the prominence of fluorene and pyrene in the subbituminous C coal sample extract.

In addition to the large difference in total extracted PAH concentrations, the PAH distribution within the high-volatile C bituminous coal sample extract is distinctly different from those of the other coal samples. For example, the substituted naphthalenes, N2-N4, are clearly the most abundant PAHs mobilized during the extraction, followed by the substituted phenanthrenes (fig. 3). The high-volatile C bituminous sample extract also contains appreciable amounts of the C_2-substituted naphthalenes, 2EtN and 1EtN, which are present at levels near or below reporting limits in the other two coal sample extracts. The high-volatile C bituminous coal sample extract contains other two-, three-, and four-ringed PAHs, including fluorene, pyrene, biphenyl, anthracene, and acenaphthene (fig. 3). With the exception of fluorene and pyrene, these other PAHs did not constitute a significant proportion of the PAHs mobilized from the other two coal samples.

Consecutive extractions of the high-volatile C bituminous coal sample continued to yield PAHs, although total PAH concentrations declined with each successive extraction. The relative concentrations of the naphthalene homologous series declined most sharply, followed by the phenanthrenes (fig. 4). Within each series, the unsubstituted homolog exhibited the most rapid decline in relative concentration, whereas the substituted homologs exhibited a more gradual decline. With the exception of the methylnaphthalenes (ΣN1), the greater the degree of substitution coincided with a more gradual decline in relative concentration during consecutive extractions.

DISCUSSION

Effect of Coal Rank

The amount and type of hydrocarbons mobilized from ground coal samples with supercritical CO_2 exhibited considerable variation with coal rank. These variations may reflect a combination of the physical and chemical changes that occur during thermal maturation (coalification) of a coal bed. The physical changes are largely reflected in both the total amount and distribution of porosity within the coal matrix in response to the increasing pressures encountered during burial. Elevated temperatures also encountered during burial promote the thermal maturation of a coal bed, resulting in the generation of discrete, or free, hydrocarbons from the organic matter in coal (e.g., Taylor and others, 1998).

Lower-rank coals typically have greater total porosity than higher-rank coals (Gan and others, 1972; Thomas and Damberger, 1976). Coal porosity is distributed among macropores (>50nm), mesopores (2-50nm), and micropores (<2nm) (IUPAC, 1982), with lower-rank coals containing a greater proportion of macropores and higher-rank coals containing a greater proportion of micropores (Gan and others, 1972). Carbon dioxide can effectively penetrate micropores (Walker, 1981). However, the amount of microporosity present within a coal bed may trap, or restrict the mobility of, hydrocarbons associated with the coal matrix (Hayatsu and others, 1978; Youtcheff and others, 1983). The combination of lower total porosity and higher proportion of microporosity typical of higher-rank coal beds may hinder hydrocarbon mobility during supercritical CO_2 injection. In this study, however, the greatest amount of hydrocarbons were mobilized from one of the higher rank (high-volatile C bituminous) coal

samples. The extent to which supercritical CO_2 mobilizes hydrocarbons from the coal matrix does not appear to be correlated to the typical variation in porosity with coal rank.

Like porosity, the amount of free hydrocarbons within the coal matrix also varies with coal rank. Initially, the free hydrocarbon content increases with coal rank, as the higher temperatures encountered during burial lead to the cracking of organic matter into smaller, discrete molecules. These molecules collectively make up a free hydrocarbon phase, i.e., bitumen, which occupies pore spaces within the coal bed. As coal rank increases further, the constituents comprising bitumen are cracked into gas, e.g., methane, molecules. The bitumen content of coal beds therefore increases to a maximum near the high-volatile bituminous coal rank, and then decreases as coal rank increases to anthracite.

Polycyclic aromatic hydrocarbons and *n*-alkanes are constituents of bitumen, and exhibit similar variations with coal rank. Using organic solvents, Allan and others (1977) found that extractable *n*-alkane content in coal samples initially increased with increasing coal rank, then declined as rank increased further. The lower rank coal samples showed preferential enrichment in the odd numbered *n*-alkanes. However, this enrichment disappeared as rank increased, and was replaced by a broad, smooth distribution of *n*-alkanes in the higher rank coal samples (Allan and others, 1977). The amount and distribution of *n*-alkanes extracted with supercritical CO_2 (fig. 1) in this study mirror these earlier findings. This similarity indicates that the chemical changes with coal rank, and the resulting effect on the amount of free hydrocarbons, strongly influences the amount of hydrocarbons mobilized with supercritical CO_2. Similar to the *n*-alkanes, Radke and others (1980) found that the amount of solvent-extractable PAHs increased with rank up through the high-volatile bituminous coal samples, and subsequently decreased as coal rank increased further. In this study, the most PAHs were extracted from the high-volatile C bituminous coal sample; lesser amounts were extracted from the subbituminous C and anthracite coal samples. These results indicate that the change in amount of available, i.e., free, hydrocarbons with coal rank is an important factor in determining the total amount of PAHs that may be mobilized during supercritical CO_2 injections.

Supercritical CO_2 mobilized appreciable amounts of hydrocarbons from the coal samples studied. However, the solubilities of individual *n*-alkanes and PAHs measured in supercritical CO_2 (McHugh and Paulaitis, 1980; Kurnik and others, 1981; Bartle and others, 1991) are significantly greater than the hydrocarbon concentrations mobilized in the extractions. This disparity may indicate that partitioning between coal and supercritical CO_2 regulates the amount of hydrocarbons mobilized, and that solubilities of individual components in supercritical CO_2 do not adequately predict the amount of hydrocarbons mobilized from coal. For example, the *n*-alkanes present in coal may be trapped within asphaltenes (Price and Clayton, 1992), a major constituent of the bitumen phase. Because asphaltenes are relatively insoluble in supercritical CO_2 (Guiliano and others, 2000), the *n*-alkanes and PAHs present within bitumen may be largely unavailable to extraction or mobilization with supercritical CO_2. As a result, the degree to which hydrocarbons are mobilized from coal samples may depend on: (1) the solubility of the hydrocarbons in supercritical CO_2 relative to bitumen, and (2) steric factors, i.e., the size of the hydrocarbon molecule relative to the physical constraints imposed by asphaltenes or the coal matrix itself. The results from consecutive extractions of a ground coal sample (figs. 2 & 4) generally show that lower molecular weight hydrocarbons are extracted more readily from coal samples than the higher molecular weight hydrocarbons. This finding supports the idea that one or both of the criteria named above affect(s) the degree to which supercritical CO_2 mobilizes hydrocarbons from coal samples.

Environmental Ramifications for CO_2 Sequestration in Deep Coal Beds

The rank of a given coal bed will influence the amount of hydrocarbons mobilized during supercritical CO_2 injection, as the amount of discrete, i.e., "available", hydrocarbons varies considerably with coal rank. As a result, coal rank is an important criterion to consider when evaluating coal beds for CO_2 storage. For example, high-volatile bituminous coal beds typically contain the highest levels of available hydrocarbons (e.g., Taylor and others, 1998), including PAHs (Radke and others, 1980), which can affect environmental quality even at relatively low concentrations. However, the more toxic PAHs, e.g., the five-ringed members such as indeno[1,2,3-cd]pyrene, and benzo[a]pyrene, do not appear to be extensively mobilized during supercritical CO_2 injection, preferring instead the coal matrix to the supercritical CO_2 phase. In this study, the most abundant PAHs mobilized during CO_2 injections are the 2- and 3-ringed members of the naphthalene and phenanthrene homologous series.

These experiments have demonstrated that injection of supercritical CO_2 into coal samples can mobilize hydrocarbons from the coal matrix under laboratory conditions. How this observed behavior will translate into field-scale CO_2 sequestration or ECBM projects depends not only on coal rank, but also on other parameters, including geologic setting, water content and time. The latter three factors have not been addressed in this study, but require consideration to fully evaluate the fate of injected CO_2 and of hydrocarbons associated with the coal matrix. The experiments conducted here are sufficiently constrained in this regard that the findings may be most representative of hydrocarbon behavior nearest the injection site (borehole) shortly after CO_2 injection has commenced.

The injection of CO_2 into a coal bed will establish a concentration gradient with higher CO_2 concentrations at the borehole and lower CO_2 concentrations further from the borehole. The interaction between this induced concentration gradient and water present in the coal bed has not been addressed here, but could have ramifications for hydrocarbon mobility in field-scale sequestration and ECBM recovery projects. Regardless of the extent to which the reservoir pressure is lowered through dewatering, a substantial amount of moisture will remain associated with the coal matrix. The moisture content of coal beds varies considerably with coal rank, ranging from 75 wt.% in lignite to 8-10 wt.% in higher rank coals (e.g., Taylor and others, 1998). Supercritical CO_2 can remove 83-96% of the moisture content from coal samples in a relatively short time period (Iwai and others, 1998). As a result, subsurface injection of supercritical CO_2 may displace water from coal beds, and the resulting supercritical CO_2-water mixtures may mobilize hydrocarbons from coal beds. For example, Ng and Bhattacharya (1987) reported that the amount of volatile matter mobilized from coal samples with supercritical CO_2 (~40°C and 148 bar) was positively correlated with water content up to 11 wt.% water. The presence of other dissolved organic compounds can greatly enhance PAH solubility in water (Gordon and Thorne, 1967). As a result, PAHs mobilized by supercritical CO_2 and supercritical CO_2-water mixtures may persist in the fluid phase even when CO_2 concentrations have diminished significantly.

The supercritical CO_2 extractions conducted in this study involved very short contact times (~ 1 h), and may only reflect CO_2-coal interactions encountered during the earliest stages of CO_2 injection into deep coal beds. In contrast, the injection phase of CO_2 sequestration-ECBM field projects will likely be much longer in duration, e.g., years (Reeves and others, 2002), and successful CO_2 sequestration projects need to "permanently" retain injected CO_2 on the scale of hundreds to thousands of years. Knowledge of CO_2-coal interactions at these time scales is beyond the scope of this study, but is essential to address the ultimate fate and environmental ramifications of injecting supercritical CO_2 into deep coal beds.

CONCLUSIONS

Experiments simulating CO_2 injection into deep coal beds have shown that supercritical CO_2 is capable of mobilizing hydrocarbons from the coal matrix. The amount and type of hydrocarbons mobilized varied in response to coal rank, with the highest concentrations of aliphatic and aromatic hydrocarbons mobilized from the high-volatile C bituminous coal sample. The coal samples continued to yield hydrocarbons during consecutive supercritical CO_2 extractions, although concentrations of extracted hydrocarbons declined with each successive extraction. Injection of CO_2 into deep coal beds, particularly at conditions near the CO_2 critical point, may displace potentially hazardous aromatic hydrocarbons from the coal matrix.

ACKNOWLEDGMENTS

REFERENCES

Allan, J., Bjorøy, M., and Douglas, A.G., 1977, Variation in the content and distribution of high molecular weight hydrocarbons in a series of coal macerals of different ranks, *in* Campos, R., and Goñi, J., eds., Advances in Geochemistry 1975: Madrid, Spain, Empresa Nacional Adaro de Investigaciones Mineras, S.A., p. 633-654.

Bartle, K.D., Clifford, A.A., Jafar, S.A., and Shilstone, G.F., 1991, Solubilities of solids and liquids of low volatility in supercritical carbon dioxide: Journal of Physical and Chemical Reference Data, v. 20, no. 4, p. 713-756.

Bustin, R.M., and Clarkson, C.R., 1998, Geological controls on coalbed methane reservoir capacity and gas content: International Journal of Coal Geology, v. 38, p. 3-26.

Gan, H., Nandi, S.P., and Walker, P.L., Jr., 1972, Nature of the porosity in American coals: Fuel, v. 51, p. 272-277.

Gentzis, T., 2000, Subsurface sequestration of carbon dioxide – an overview from an Alberta (Canada) perspective: International Journal of Coal Geology, v. 43, p. 287-305.

Gluskoter, H., Stanton, R.W., Flores, R.M., and Warwick, P.D., 2002, Adsorption of carbon dioxide and methane in low-rank coals and the potential for sequestration of carbon dioxide: Environmental Geosciences, v. 9, no. 3, p. 160-161.

Gordon, J.E., and Thorne, R.L., 1967, Salt effects on non-electrolyte activity coefficients in mixed aqueous electrolyte solutions –II. Artificial and natural sea waters: *Geochimica et Cosmochimica Acta*, v. 31, no. 12, p. 2433-2443.

Guiliano, M., Boukir, A., Doumenq, P., Mille, G., Crampon, C., Badens, E., and Charbit, G., 2000, Supercritical fluid extraction of Bal 150 crude oil asphaltenes: Energy & Fuels, v. 14, no. 1, p. 89-94.

Hayatsu, R., Winans, R.E., Scott, R.G., Moore, L.P., and Studier, M.H., 1978, Trapped organic compounds and aromatic units in coals: Fuel, v. 57, p. 541-548.

Herzog, H.J., 2001, What future for carbon capture and sequestration? New technologies could reduce carbon dioxide emissions to the atmosphere while still allowing the use of fossil fuels: Environmental Science and Technology, v. 35, no. 7, p. 148A-153A.

IUPAC, 1982, Manual of symbols and terminology, Appendix 2, Part 1. Colloid and surface chemistry: Pure and Applied Chemistry, v. 52, p. 2201.

Iwai, Y., Amiya, M., Murozono, T., Arai, Y., and Sakanishi, K., 1998, Drying of coals by using supercritical carbon dioxide: Industrial & Engineering Chemistry Research, v. 37, no. 7, p. 2893-2896.

Karacan, C.O., 2003, Heterogeneous sorption and swelling in a confined and stressed coal during CO_2 Injection: Energy&Fuels, v. 17, p. 1595-1608.

Kolak, J.J., and Burruss, R.C., 2003, An organic geochemical assessment of CO_2-coal interactions during sequestration: Proceedings, Second Annual Conference on Carbon Sequestration, May 5-8, 2003, Alexandria, VA, USA [unpaginated CD-ROM].

Klusman, R.W., 2003, Rate measurements and detection of gas microseepage to the atmosphere from an enhanced oil recovery/sequestration project, Rangely, CO, USA: Applied Geochemistry, v. 18, p. 1825-1838.

Krooss, B.M., van Bergen, F., Gensterblum, Y., Siemons, N., Pagnier, H.J.M., and David, P., 2002, High-pressure methane and carbon dioxide adsorption isotherms on dry and moisture-equilibrated Pennsylvanian coals: International Journal of Coal Geology, v. 51, p. 69-92.

Kurnik, R.T., Holla, S.J., and Reid, R.C., 1981, Solubility of solids in supercritical carbon dioxide and Ethylene: Journal of Chemical Engineering Data, v. 26, p. 47-51.

McHugh, M., and Paulaitis, M.E., 1980, Solid solubilities of naphthalene and biphenyl in supercritical carbon dioxide: Journal of Chemical Engineering Data, v. 25, no. 4, p. 326-329.

Monin, J.C., Barth, D., Perrut, M., Espitalie M., and Durand B., 1988, Extraction of hydrocarbons from sedimentary rocks by supercritical carbon dioxide: Organic Geochemistry, v. 13, no. 4-6, p. 1079-1086.

Ng, S.H., and Bhattacharya, S.N., 1987, Transport characteristics of coal-liquid CO_2 suspensions, *in* Moulijn, J.A., Nater, K.A., and Chermin, H.A.G., eds., 1987 International Conference on Coal Science: Elsevier, Amsterdam, The Netherlands, p. 491-494.

Pashin, J.C., and McIntyre, M.R., 2003, Temperature-pressure conditions in coalbed methane reservoirs of the Black Warrior basin: implications for carbon sequestration and enhanced coalbed methane recovery: International Journal of Coal Geology, v. 54, p. 167-183.

Price, L.C., and Clayton, J.L., 1992, Extraction of whole versus ground source rocks: Fundamental petroleum geochemical implications including oil-source rock correlation: Geochimica et Cosmochimica Acta, v. 56, p. 1213-1222.

Radke, M., Schaefer, R.G., Leythauser, D., 1980, Composition of soluble organic matter in coals: relation to rank and liptinite fluorescence: Geochimica et Cosmochimica Acta, v. 44, p. 1787-1800.

Reeves, S.R., Clarkson, C., and Erickson, D., 2002, Selected field practices for ECBM recovery and CO_2 sequestration in coals based on experience gained at the Allison and Tiffany Units, San Juan basin: DOE Topical Report DE-FC26-00NT40924, available at http://www.coal-seq.com/Proceedings/Field_Report.pdf .

Taylor, G.H., Teichmüller, M., Davis, A., Diessel, C.F.K., Littke, R., and Robert, P., 1998, Organic Petrology: Berlin, Germany, Gebrüder Borntraeger, 704 p.

Thomas, J., Jr., and Damberger, H.H., 1976, Internal surface area, moisture content, and porosity of Illinois coals: Variations with coal rank: Illinois State Geological Survey Circular 493, 38 p.

Walker, P.L., Jr., 1981, Microporosity in coal: its characterization and its implications for coal utilization: Philosophical Transactions of the Royal Society of London A, v. 300, p. 65-81.

Warwick, P.D., Barker, C.E., SanFilipo, J.R., and Morris, L.E., 2000, Preliminary results from coal-bed methane drilling in Panola County, Texas: U.S. Geological Survey Open-File Report 00-048, 30 p.

Warwick, P.D., Barker, C.E., and SanFilipo, J.R., 2002, Preliminary evaluation of the coalbed methane potential of the Gulf Coastal Plain, USA and Mexico, *in* Schwochow, S.D., and Nuccio, V.F., eds., Coalbed Methane of North America, II: Denver, CO, Rocky Mountain Association of Geologists, p. 99-107.

Youtcheff, J.S., Given, P.H., Baset, Z., and Sundaram, M.S., 1983, The mode of association of alkanes with coals: Organic Geochemistry, v. 5, no. 3, p. 157-164.

Table 1. Results of the proximate, ultimate, and petrographic analyses for the coal samples presented in this paper.

Sample Name	PA-2-CN2	20011006 A3	PAS-1224
Location	Gulf Coast *(Texas)*	Illinois basin *(Indiana)*	Appalachian basin *(Pennsylvania)*
Coal Rank	subbituminous C	high-volatile C bituminous	anthracite

Proximate, as-received basis

Btu/lb	8006	11916	12052
Ash %	11.11	5.52	10.16
Moisture %	30.87	11.78	7.98
Sulfur %	0.53	0.62	0.94
Fixed Carbon	29.44	45.79	75.11
Btu/lb, MMMF[*]	9098	12684	13563
Fixed Carbon, DMMF[†]	51.65	55.79	93.09

Ultimate, as-received basis

Hydrogen %	6.43	5.33	2.75
Carbon %	46.59	69.35	75.36
Nitrogen %	1.04	1.40	0.71
Sulfur %	0.53	0.53	0.94
Oxygen %	37.73	17.90	10.08
Ash %	11.11	5.49	10.16
Free Swelling Index	0	NA[‡]	0
Apparent Specific Gravity (g cm^{-3})	1.37	NA[‡]	1.53

Petrography
Maceral Content

Vitrinite (%)	53.6	91	83
Liptinite (%)	8.8	4.4	0
Inertinite (%)	36.4	4.4	7

Ro (%)	0.45	0.59	4.14

[*]MMMF: *moist, mineral-matter free*
[†]DMMF: *dry, mineral-matter free*
[‡]NA: *not analyzed*

Table 2. Roster of PAH Compounds and Corresponding Target Ions Used in GC-MS Analyses*.

| Analyte	Abbreviation	Target Ion (m/z)
naphthalene	N0	128
1-benzothiophene	1BT	134
1-methylnaphthalene & 2-methylnaphthalene	ΣN1	142
biphenyl	Bip	154
1-ethylnaphthalene	1EtN	141
2-ethylnaphthalene	2EtN	141
2,6-dimethylnaphthalene	ΣN2	156
acenaphthylene	Acey	152
acenaphthene	Acen	153
2,3,5-trimethylnaphthalene	ΣN3	170
fluorene	F0	166
1,2,5,6-tetramethylnaphthalene	ΣN4	184
dibenzothiophene	DBT	184
phenanthrene	P0	178
anthracene	Ant	178
1-methylphenanthrene	ΣP1	192
3,6-dimethylphenanthrene	ΣP2	206
fluoranthene	Flu	202
pyrene	Pyr	202
1,2,4-trimethylphenanthrene	ΣP3	220
benz[a]anthracene	B[a]a	228
chrysene	C0	228
benzo[b]fluoranthene	B[b]f	252
benzo[k]fluoranthene	B[k]f	252
benzo[e]pyrene	B[e]p	252
benzo[a]pyrene	B[a]p	252
perylene	Per	252
indeno[1,2,3-cd]pyrene	Icp	276
dibenz[a,h]anthracene	Dba	278
benzo[ghi]perylene	Bgp	276

The shaded entries indicate where the calibration curve for a single analyte was used to determine the total concentration (Σ) of all corresponding isomers.
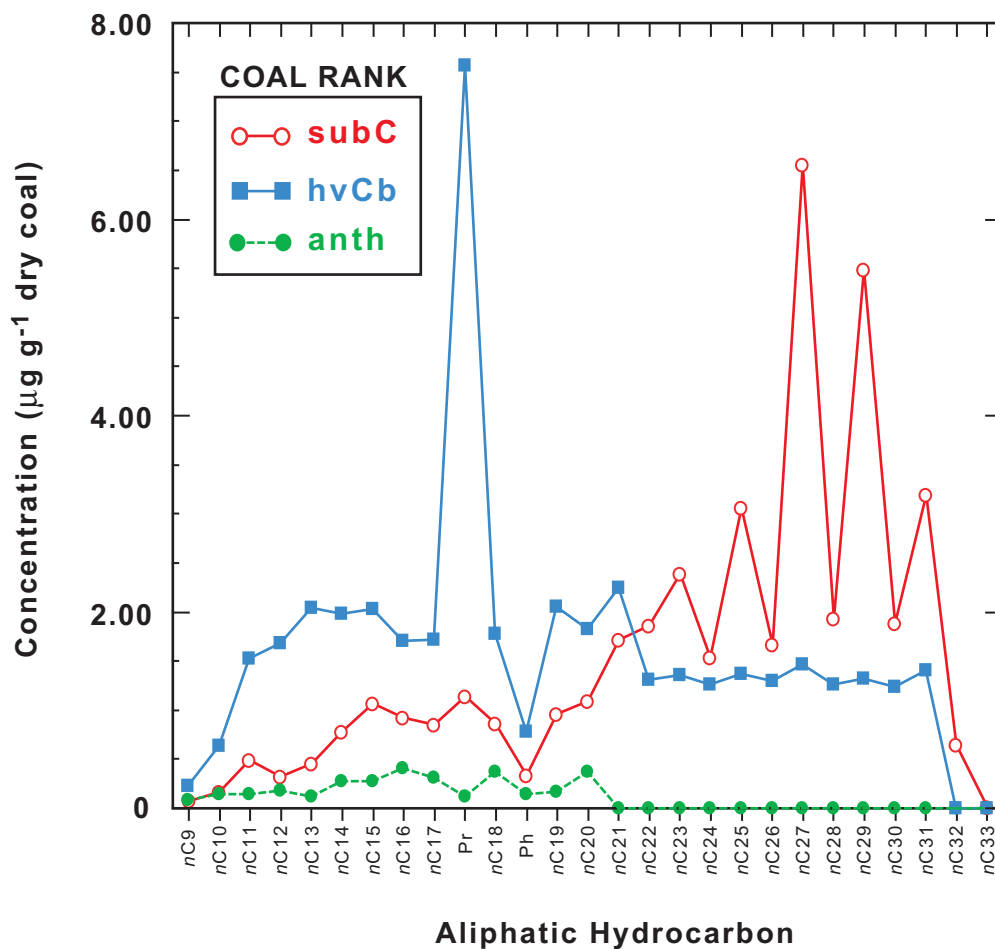
Figure 1. Concentrations of target aliphatic compounds in supercritical CO_2 extracts from ground coal samples.
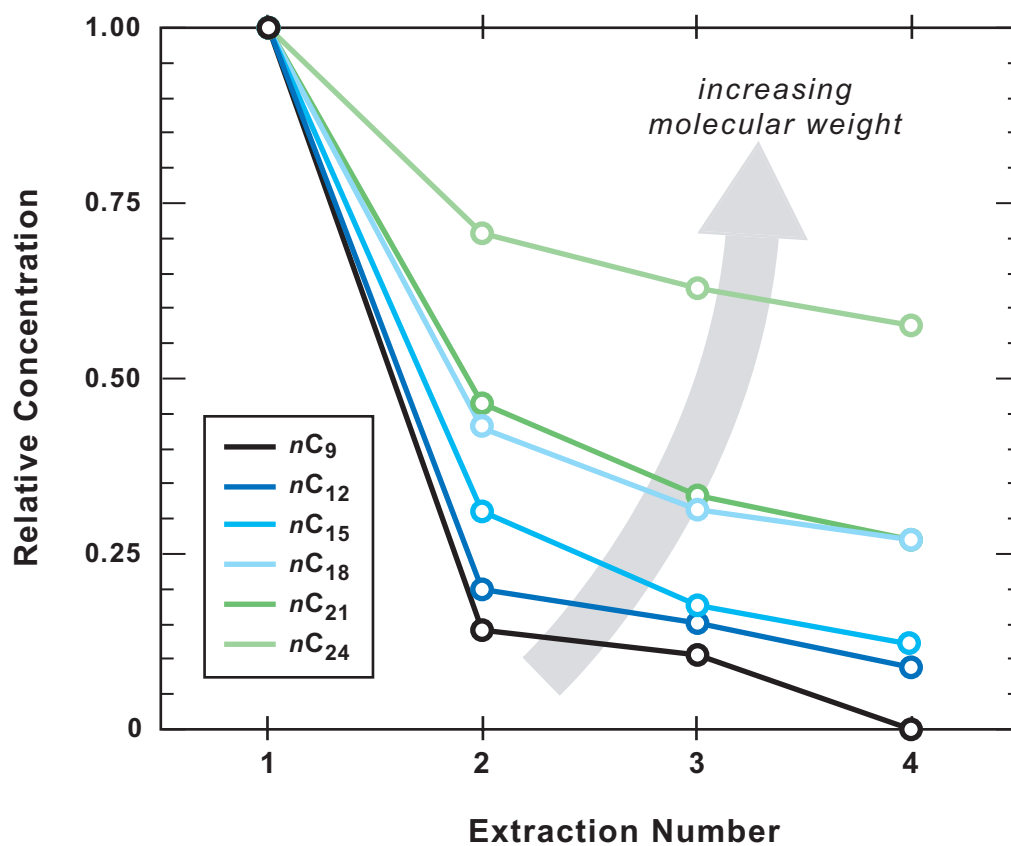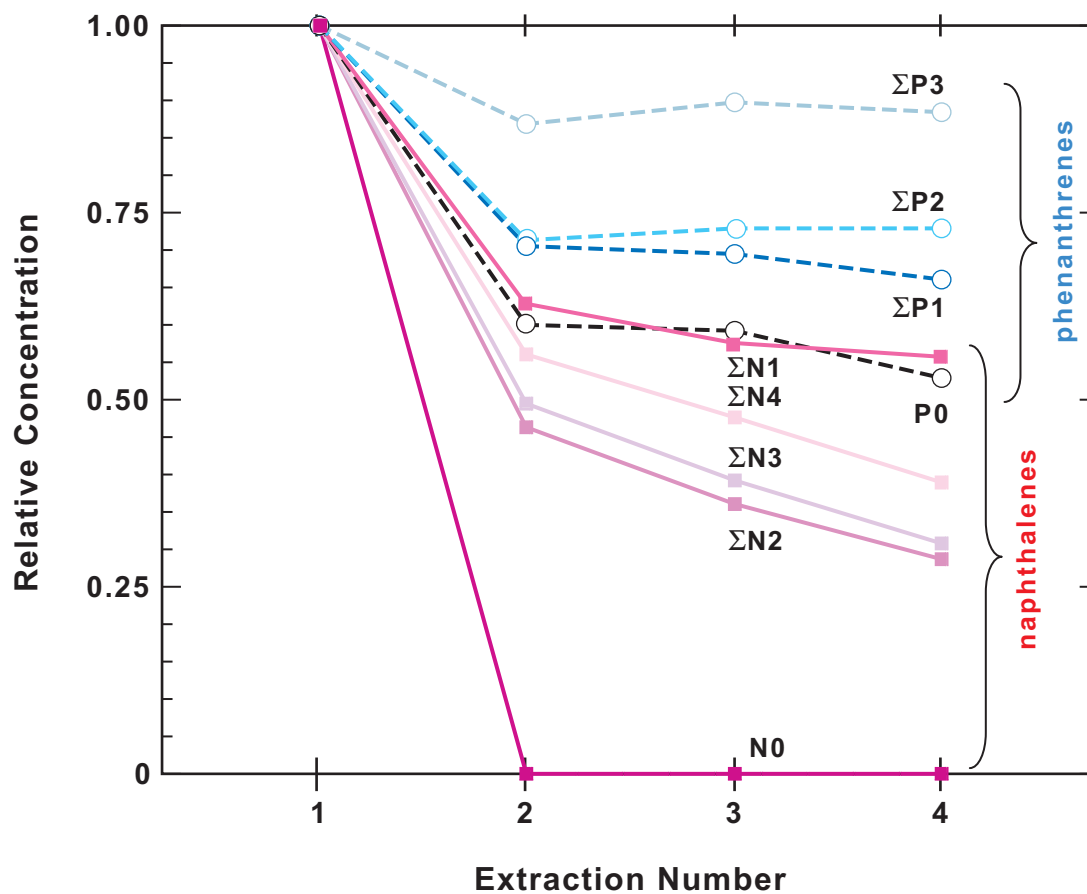
Figure 2. Relative concentrations of selected aliphatic compounds in consecutive supercritical CO_2 extracts from a ground coal sample (hvCb).
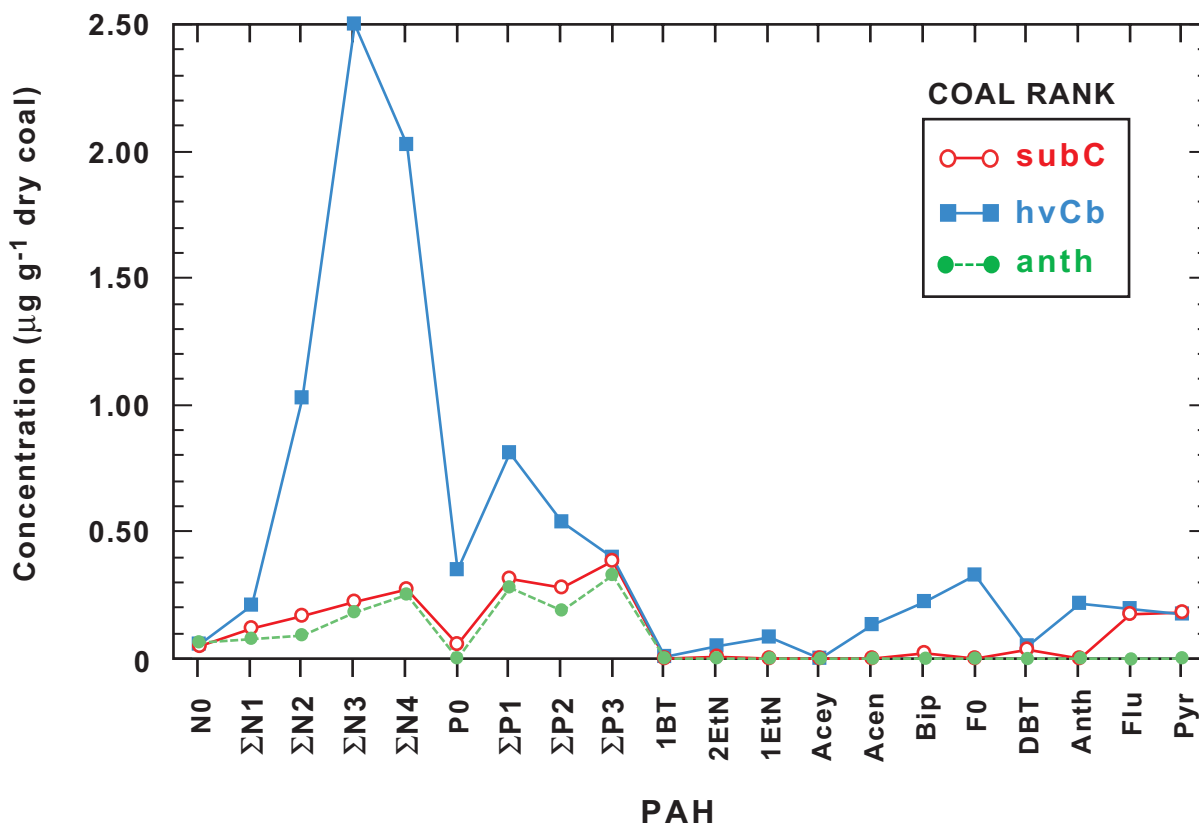
Figure 3. Concentrations of PAH compounds in supercritical CO_2 extracts from ground coal samples. Larger PAH compounds, e.g., B[b]f and Icp, were detected in the subbituminous C coal sample extract, but at levels below reporting limits.

Figure 4. Relative concentrations of selected PAHs in consecutive supercritical CO_2 extracts from a ground coal sample (hvCb).